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Pulsed laser deposited Y-doped $BaZrO_3$ thin films for high temperature humidity sensors

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ABSTRACT

Pulsed laser deposited (PLD) Y-doped $BaZrO_3$ thin films ($BaZr_{1-x}Y_xO_{3-y/2}$, $x = 0.2$, $y > 0$), were investigated as to their viability for reliable humidity microsensors with long-term stability at high operating temperatures ($T > 500\,^{\circ}C$) as required for in situ point of source emissions control as used in power plant combustion processes. Defect chemistry based models and initial experimental results in recent humidity sensor literature [1,2]. indicate that bulk Y-doped $BaZrO_3$ could be suitable for use in highly selective, high temperature compatible humidity sensors. In order to accomplish faster response and leverage low cost batch microfabrication technologies we have developed thin film deposition processes, characterized layer properties, fabricated and tested high temperature humidity micro sensors using these thin films. Previously published results on sputtering Y-doped $BaZrO_3$ thin films have confirmed the principle validity of our approach [3]. However, the difficulty in controlling the stoichiometry of the films and their electrical properties as well as mud flat cracking of the films occurring either at films thicker than 400 nm or at annealing temperature above 800 °C have rendered sputtering a difficult process for the fabrication of reproducible and reliable thin film high temperature humidity microsensors, leading to the evaluation of PLD as alternative deposition method for these films.

X-ray Photoelectron Spectroscopy (XPS) data was collected from as deposited samples at the sample surface as well as after 4 min of Ar^+ etching. PLD samples were close to the desired stoichiometry. X-ray diffraction (XRD) spectra from all as deposited $BaZrO_3$:Y films show that the material is polycrystalline when deposited at substrate temperatures of 800 °C. AFM results revealed that PLD samples have a particle size between 32 nm and 72 nm and root mean square (RMS) roughness between 0.2 nm and 1.2 nm. The film conductivity increases as a function of temperature (from 200 °C to 650 °C) and upon exposure to a humid atmosphere, supporting our hypothesis of a proton conduction based conduction and sensing mechanism. Humidity measurements are presented for 200–500 nm thick films from 500 °C to 650 °C at vapor pressures of between 0.05 and 0.5 atm, with 0.03–2% error in repeatability and 1.2–15.7% error in hysteresis during cycling for over 2 h. Sensitivities of up to 7.5 atm^{-1} for 200 nm thick PLD samples at 0.058 atm partial pressure of water were measured.

1. Introduction

Power generation using fossil fuels generally involves high temperature and high pressure. Associated with any type of power generation using fossil fuels is formation of some gaseous species, such as H_2O, CO, CO_2, NH_3, H_2, etc. Today, there is no single mechanism, material, or operating mode will be fit to provide the requirements of the restrictions on emissions from fossil fuel fired power plants and internal combustion engines [4]. Microscale (MEMS) gas sensing devices are being developed to help monitor emissions and provide feedback for advanced engine controls and emission control devices. In order to help accurately measure the concentrations of all gaseous species present in the exhaust gas, the reliable measurement of water vapor partial pressure that is produced in the combustion process is necessary. In addition, water vapor can influence the measurement of Combustion exhaust gas when using, e.g. metal oxide sensors such as In_2O_3 at a high operating temperatures ($T > 200\,^{\circ}C$), [5].

Several humidity sensors based on surface adsorption of water vapor (H_2O) have been reported [6–9]. These humidity sensors lack selectivity towards NO_x and O_2, as well as typically featuring low operating temperature ranges of between 20 °C and 95 °C making them unsuitable for the use in exhaust gas streams [10–13]. An alternative sensing mechanism based on absorption of H_2O into

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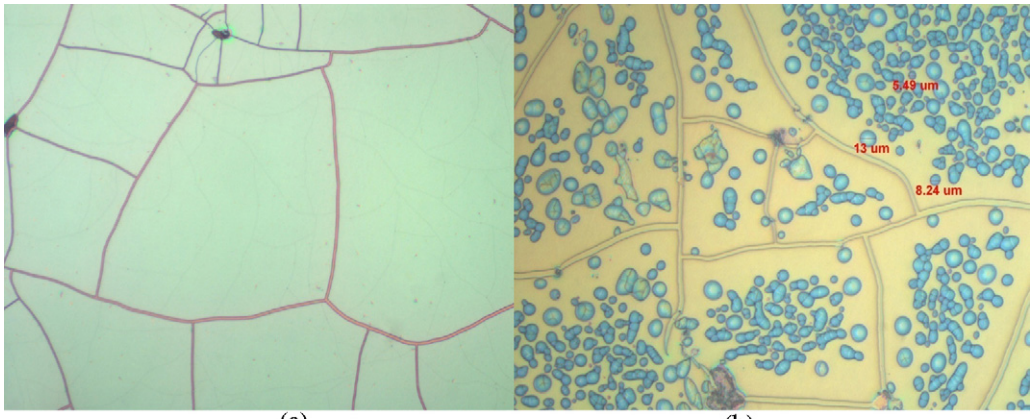

Fig. 1. Microscopy 6× pictures of cracked sputtered thin film with a film thickness of 400 nm (a) annealed at 800 °C in air for 3 h and (b) annealed at 1000 °C in air for 3 h.

the lattice, provides better selectivity since only selected species present in the combustion gas readily dissolve into the solid lattice [3]. $BaZrO_3$ is a ceramic material with Perovskite structure that has been reported to have high chemical stability at high operating temperatures (i.e. it does not (permanently) change its basic chemical composition and structure, when exposed to other gaseous species) and high proton conductivity when doped appropriately [14–15]. When doped with a lower valent ion on the Zr-site, the material contains oxygen vacancies and can exhibit oxygen ion conductivity [1]. The material can also feature *p*-type electronic conductivity in atmospheres with high oxygen partial pressure [1]. At temperatures $T > 500\,^{\circ}C$, H_2O dissolves into the lattice thus "filling in" the oxygen vacancies and releasing protons into the structure. Such defect chemistry allows a repeatable, selective, and sensitive sensing mechanism [16–20]. By fabricating and testing high temperature humidity micro sensors using thin films we could not only significantly reduce response time, but also allow for low cost fabrication, which would allow transfer of the technology into higher volume markets, such as, e.g. automotive and combustion engine management.

Previously published results on sputtered Y-doped $BaZrO_3$ thin films have confirmed the principle validity of our approach [3]. However (1) the difficulty in controlling the stoichiometry of the films and their electrical properties as well as (2) mud flat cracking of the films (Fig. 1) occurring at films thicker than 400 nm or when annealing at temperatures above 800 °C have rendered sputtering a difficult process for the use in reproducible and reliable fabrication of thin film humidity microsensors for operating temperatures above 500 °C.

This work presents pulsed laser deposition (PLD) as alternative high temperature deposition method for Y-doped $BaZrO_3$ thin films, allowing the potential mitigation of the above stated drawbacks of sputtered films problems while maintaining the advantageous humidity sensing characteristics of the films.

2. Experimental methods

Y-doped $BaZrO_3$ of 200, 300, 400, and 500 nm thin films were deposited onto oxidized 2″ *n*-type (1 0 0) silicon substrates using PLD at substrate temperatures of 800 °C in a vacuum ambient with base pressure at 8.5×10^{-7} Torr. Films were characterized using X-Ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD), and Atomic Force Microscopy (AFM), to determine film composition, microstructure, and surface morphology. Electrical conductivity as function of temperature and water vapor humidity sensing characteristics of the films were measured using a custom-built gas sensor test station that up to 650 °C. Silicon based gas sensor test structures with Cr (20 nm) and Au (180 nm) thin film metallization deposited on top of the sensing material were fabricated for humidity tests as previously published [3]. The size of each sensor is $7 \times 7\ mm^2$.It uses 10 pairs of interdigitated electrodes (IDE) spaced 100 μm apart and includes a resistive thin film heater, a resistive temperature device (RTD), and the sensitive layer.

2.1. Characterization of film composition and structure

The electroceramic thin films were deposited by pulsed-laser deposition from a 1″ diameter, 99.9% pure ceramic $BaZr_{0.8}Y_{0.2}O_{2.9}$ pure ceramic target purchased from Process Materials Inc. The chemical composition of the target was studied with X-ray fluorescence (XRF) by Evans Analytical Group (EAG) exhibiting a larger Y concentration (7%) than expected (4%). The films were deposited on oxidized 2″ *n*-type (1 0 0) silicon substrates at 800 °C substrate temperature and a base pressure of 8.5×10^{-7} Torr in a PVD products Inc system. The films were grown at 50 Hz, 250 mJ/pulse laser energy with average energy flux of $1\ J/cm^2$, yielding a film thickness uniformity of ±10%. Films with a center thickness of 200, 300, 400, and 500 nm were deposited. Since the PLD process only allows for limited area of uniform thickness, the center thickness constitutes the target film thickness. Towards the edge of the substrate the film thickness can drop by 16–22%. Thicknesses were verified using a Woolam V-Vase spectroscopic ellipsometer. X-ray photoelectron spectroscopy (XPS) measurements were made using a Kratos Axis ULTRA^{DLD} system using monochromatic Al Kα radiation. Composition data was recorded for as received samples and after 4 min of Ar^+ ion beam etching. X-ray diffraction (XRD) measurements were made using a Philips X'Pert system using Cu Kα radiation in the Bragg-Brentano geometry for 2θ angles from 10–90°. Atomic force microscopy (AFM) micrographs were collected with a Veeco Dimension 3000 system using etched Si tapping mode tips with a nominal tip radius of ∼5 nm.

2.2. Water vapor sensitivity measurements

The water vapor sensing characteristics for PLD $BaZrO_3$:Y thin films were measured using a custom-built gas sensor test station. Sample chips were placed on a hotplate in a stainless steel chamber and contacted with probe needles attached to a PC/labview controlled Keithley digital multimeter in voltage measurement mode. N_2 carrier gas at 200 sccm was passed through a water bubbler at 80 °C, saturating the gas at 0.468 atm water vapor pressure. N_2 as opposed to compressed air was chosen as carrier gas for this initial set of experiments, in order to (1) establish the baseline characteristics for the sensitive layer without impact from potential chemical